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MODELLING OF EFFICIENCIES IN BIOGAS PLANTS WITH CONSIDERATION OF INCOMPLETE MASS AND ENERGY BALANCES BASED ON CALORIMETRIC INVESTIGATIONS AND DATA SAMPLING - DEVELOPING A NEW MANAGEMENT TOOL SYSTEM

BY
RENÉ CASARETTO

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Preface:

This Ph.D. dissertation entitled "Modelling of efficiencies in biogas plants with consideration of incomplete mass- and energy balances based on calorimetric investigations and data sampling - Developing a new management tool system" has been submitted to the Doctoral School of Aalborg University, in partial fulfillment of the requirement for the Ph.D. degree.

The majority of the work was carried out at the Department of Energy Technology, Aalborg University Campus Esbjerg and University of Applied Sciences Flensburg as part of the Large Scale Bioenergy Laboratory 2, funded by INTERREG 5a, from August 2016 to May 2019.

This Ph.D. study is supervised by Professor Jens Bo Holm-Nielsen and Professor Jens Born.

The dissertation is based on the works prepared in the following manuscripts referred by their Arabic number in the text.

1. Casaretto, R., Thomsen, F., Born, J., Holm-Nielsen, J.B. (2019). Lignin Analysis Methods – Usage as efficiency indicator for commercial scale biogas plants in comparison with traditional methods, *Bioresource Technology Reports,* *https://doi.org/10.1016/j.biteb.2019.100201*
2. Casaretto, R., Lassen Agdal, E.B. , Cayenne, A., Chaturvedi, T., Born, J., Holm-Nielsen, J.B., (2019). Low temperature pretreatment of lignocellulosic biomass for enhanced biogas production, *Chemical Engineering & Technology – Submitted Manuscript*
3. Casaretto, R., Mächtig, T., Moschner, C.R., Hartung, E., Born, J., Holm-Nielsen, J.B., (2019), Examining anaerobic biodegradability of digestates –influence of and correlations for Klason-lignin, *Chemical Engineering & Technology – Submitted Manuscript – Revised - In Press*

In addition the following publications were produced – in preparation – during the PhD study:

4. Casaretto, R., Born, J., Holm-Nielsen, J.B., (2019), Comparison of biogas plants by their input materials and plant design – In preparation - Draft
5. Boggula, R.R., Fischer, D., Casaretto, R., Born, J., (2019), Methanation Potential: Suitable catalyst and optimized process conditions for upgrading Biogas to reach gas grid requirements, *Biomass and Bioenergy – Submitted Manuscript*

Oral presentations on conferences, seminars and congresses:

René Casaretto, Jens Born, Jens Bo Holm-Nielsen, “Efficiency of commercial scale biogas plants by time series analysis”, International Conference Progress in Biogas, Hohenheim University, 09.03.2017

René Casaretto, Jens Born, Jens Bo Holm-Nielsen, “Energy Efficiency of commercial scale biogas plants by time series analysis”, New Energy Fair Conference, Husum, 17.03.2017

René Casaretto, Jens Born, Jens Bo Holm-Nielsen, “Efficiency of biogas plants by time series analysis”, 3rd Conference on Monitoring and Process Control of Anaerobic Digestion Plants, Leipzig, 29.03.2017

René Casaretto, Jens Born, Jens Bo Holm-Nielsen, Evaluation and Modelling the Energy Efficiency of Commercial Scale Biogas Plants” EUBCE 2017, Stockholm, 12 – 16.06.2017

René Casaretto, Jens Bo Holm-Nielsen, Jens Born, “Designing a biogas plant – which factors are relevant and how can we measure them?, Nutrifair 2019, Middelfart, 16-17.01.2019

Torsten Stefan, René Casaretto, Jens Bo Holm-Nielsen, Eberhardt Hartung, Jens Born, „Prediction of Klason lignin in digestates by calorimetry”, 4th Conference on Monitoring and Process Control of Anaerobic Digestion Plants, Leipzig, 26-27.03.2019

Emil Brohus Lassen Agdal, René Casaretto, Jens Bo Holm-Nielsen, “Biomethane and Technical CO2 supply in Denmark - The Korskro case, Esbjerg” – Regatec 2019, Malmö,
20 – 21.05.2019

Poster Presentations:

René Casaretto, Jens Bo Holm-Nielsen, Jens Born, “Evaluation and modelling the energy efficiency of commercial scale biogas plants”, European Biomass Conference and Exhibition, 12.-16.06.2017, Stockholm Sweden”

Emil Brohus Lassen Agdal, René Casaretto, Jens Born, Jens Bo Holm-Nielsen, “Light cooking of lignocellulosic biomass as a cheap pre-treatment for Increased biogas production”, 4th Conference on Monitoring & Process Control of Anaerobic Digestion Plants

This thesis has been submitted for assessment in the partial fulfillment of the Ph.D. degree. The thesis is based on the submitted or published scientific papers which are listed above. Parts of the papers are used directly or indirectly in the extended summary of the thesis. In its present form the thesis cannot be openly published, but only so in limited and closed circulation as copyright may not be ensured.

René Casaretto

Table of contents

Modelling of efficiencies in biogas plants with consideration of incomplete mass and energy balances based on calorimetric investigations and data sampling - Developing a new management tool system

Abstract

Biogas production from agricultural waste streams and energy crops provides several different value streams: production of green energy by using waste streams, reduced greenhouse gas emissions (GHG) and production of nutrient rich digestates as fertilizer.

On the other side, commercial scale biogas plants are mostly installed to be economically profitable. This leads to the main focus point in biogas production: The energy efficiency of these plants. Previous research has identified several different methods for determining the energy efficiency of commercial scale biogas plants. These methods are mainly based on biomethane potential tests (BMP), elementary compound analysis and historical observations.

One of the main problems for determining the efficiency is the lack of data – incomplete mass- and energy balances. This is caused by the insufficient measuring technologies, which are available for large (farm) scale biogas plants, and also have to be as cheap as possible.

The aim of this work is to implement a new modelling systematics for determining the energy efficiency with incomplete mass- and energy balances.

For this, commercial scale biogas plants have been investigated for two years and samples from the input and output materials were taken and analyzed for the dry material (DM), organic dry material (oDM), volatile fatty acids (VFA) and the gross calorific value (GCV). For mass and energy balances the production data of each biogas plant were used, the balance borders were set around the first fermenter and the last gas tight tank of the system.

The results revealed large variations in the efficiency of Danish and German biogas plants with consistent correlations between input materials, retention time, residual energy content and gas production.

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At first, I want to express my great gratitude to my supervisors, Jens Bo Holm-Nielsen and Jens Born, for all their trust and help during my PhD studies. Thank you for giving me the opportunity to write my doctoral thesis. You always inspired me with new ideas, encouraged me, and were willing to spend your time to discuss, to give me suggestions on my research works – even if they sometimes ended in a dead end.

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Many thanks to my collaborators at University of Applied Sciences Flensburg – Martina Carstensen, Aadila Cayenne and Fritz Thomsen, my good colleague at University of Kiel, Torsten Mächtig who always presented a solution, even if there was no way visible on the road. Special thanks to my good friend Julius Kruse, who always discussed all problems even at night-time. Also I want to thank my “mental mentor” – René Fabian – who teached me to be “calm” in hard situations.

At the end, I would like to say a huge thanks to my family for supporting and understanding me all the time. Thanks to my Dad, who always trusted me on my ideas. Great thanks to my son, Julius, and my daughter Hanna – the love of my life – who guided me through the way and encouraged me with her lovely smile.

René Casaretto – October 2019

List of figures and tables

Abbreviations

ABL	Acid Bromide Lignin
AD	Anaerobic digestion
ADL	Acid detergent lignin
BMP	Biochemical methane potential
CHP	Combined Heat and Power Plant
C/N	Carbon / Nitrogen ratio
CSTR	Continuous stirred tank reactor
DM	Dry Material
FM	Fresh matter
GHG	Greenhouse gas
GCV	Gross calorific value
HRT	Hydraulic retention time
HTC	Hydro-Thermal Carbonization
RE	Renewable Energies
RED-II	Renewable Energy Directive II
RER	Renewable Resources
Res	Fermentation Residues
KL	Klason Lignin
M	Manure
ORC	Organic Rancine Cycle
PJ	Peta Joule
tKL	total Klason-Lignin
TKN	Total Kjieldahl nitrogen
TS	Total Solids
VFA	Volatile fatty acids
VS	Volatile Solids
WS	Wheat Straw

Summary (in English)

Anaerobic digestion (AD) of lignocellulosic biomass, such as agricultural residues or energy crops, can produce green and sustainable energy as in form of biogas. In practice, several challenges have appeared by the generation of biogas from these resources – As such, the biodegradability of these materials with AD plants is limited by the protective structures of the lignocellulosic biomass, which is resistant to microbial or enzymatic degradation. Secondly, the existing AD plants are related to traditional wastewater treatment plants and do not have the opportunity to degrade high solid contents and / or biomass with high lignin contents.
On the other hand, there is the need for existing biogas plants to generate biogas from cheap and broadly available resources.

The aim of this PhD study was to investigate commercial scale biogas plants in Germany and Denmark by their energy efficiency and to generate an independent energy efficiency factor apart from biodegradability which takes the anaerobic available and non-available (lignin) contents into account. For this, time-series-analysis were performed taking the produced energy and used input materials into account. By this, the main problem was related to incomplete mass and energy balances. The mass balance is incomplete by the fact, that biogas plants normally not weight every tank wagon which has left the plant and secondly that the rain and leachate water is not measured sufficiently. Energy balances were incomplete, because of unspecific losses (roofs, concrete, feeding systems and pressure safety valves). Furthermore, improving the economics with cheap and easy pretreatment methods for lignocellulosic biomass (wheat straw) was investigated.

In one study, different biogas plants were investigated by a one-year time series analysis for their energy efficiency – for this the

input and output materials were investigated and the total energy content was measured by the gross calorific value (GCV). In general, the total energy efficiency could be conducted by the GCV method, but there was no possibility to differentiate between anaerobic degradable and non-degradable parts with this method. However, the presented methodology allows independent economic statements for each AD plant. This is possible because the energetic consideration of the upper limit (maximum of possible energy generation by combustion) sets a benchmark. By comparing the residual energy content of the digestates with the input material energy mix, an AD-plant specific energy efficiency is presented which allows to estimate the economic effect of pretreatment or extension of hydraulic retention time.

In the second study, thirty-four digestates from biogas plants were investigated with respect to their basic compounds, GCV, residual Biomethane potential and Klason-Lignin-content (tKL) in order to find correlations between tKL and GCV and the possibility to predict the BMP with GCV. To find cross-correlations, statistical methods were used. For this, multivariate linear models and multivariate models (PLS) were used. However, the results of this study showed, that no clear correlations were visible and that 1.) the Klason –extraction - method had not been developed for digestates, 2.) that the GCV methods seems not to be sensitive enough to highlight small differences between the different relations of the substrate mixture.

Beside digestion, AD can also benefit from pretreatment for enhanced biogas production / methane production. For this a third study was carried out on light cooking as a cheap and easy pretreatment method for enhanced biogas production from wheat straw. For this, wheat straw was pretreated in water / digestates at different temperatures (293 – 372 K) and different holding times (30 – 60 minutes). The aim was to figure out the highest BMP by removing protective structures, such as wax layers to enable hydrolysis of the material. Best results were found by pre-soaking under ambient conditions. In general, the statement can be formulated, that with pre-soaking in water, higher BMP can be expected. This effect can be related to two effects, 1.) light cooking in water removes a part of the protective wax layer, so that the microbiology can degrade the protected structures, e.g. cellulose. 2.) pre-soaking in water dissolves the bound salts from the structure and as a result of it, compared with light cooking in digestates, higher BMP was conducted.

Resumé (På Dansk)

Den anaerobe gæring af træfiber-rige biomasse, såsom landbrugs rester eller energiafgrøder, kan producere grøn og bæredygtig energi i form af biogas. I praksis er der mange udfordringer i produktionen af biogas fra disse ressourcer, da disse råvarers bionedbrydelighed er begrænset af biogasprocessen. Dette skyldes de beskyttende strukturer af biomassen, som er resistente over for mikrobiel eller Enzymatisk nedbrydning. Desuden er de eksisterende biogasanlæg afledt af konventionelle rensningsanlæg og er derfor ikke i stand til at fermentering af højt tørstofindhold effektivt. På den anden side er der et økonomisk behov for at producere billig og bæredygtig biogas fra billige og alment tilgængelige ressourcer.

Formålet med denne doktorafhandling var at undersøge store biogasanlæg i Tyskland og Danmark med hensyn til deres energieffektivitet og at udvikle en uafhængig effektivitetsfaktor ud over de materialers bionedbrydelighed, som den anaerobe tilgængelige ingredienser i gærings rester. Til dette formål blev der udført tidsserieanalyser under hensyntagen til de genererede energistrømme og inputmaterialer. Utilstrækkelig måleteknologi er blevet identificeret som det største problem for korrekt bogføring. For det meste registreres de flydende gærings rester ikke ved en kalibreret skala, men hvis det overhovedet er, registreres antallet af tankskibe. Desuden registreres perkolat og regnvand ikke i bulk på planterne.

Energibalancen er ufuldstændig på grund af ikke-specifikke tab, såsom gasgennemtrængning over tagene, gennemtrængning via beton, tab i rør og overtryks sikringer. Desuden blev forbedringen af anlæggenes effektivitet ved hjælp af omkostningseffektive og enkle forbehandlingsmetoder for lignocellulose rige råmaterialer som hvede halm undersøgt.

I en undersøgelse blev forskellige biogasanlæg undersøgt for deres energieffektivitet over en etårig tidsserieanalyse – til dette formål blev input-og output materialerne undersøgt og evalueret i forhold til brændværdi (GCV). Generelt kan energimæssig ydeevne bestemmes ved hjælp af GCV-metoden, men der er i øjeblikket ingen måde at skelne mellem nedbrydelig og ikke-nedbrydelig andel med denne metode. Den fremlagte metodologi giver dog mulighed for en uafhængig økonomisk vurdering for hvert biogasanlæg. Dette er muligt, fordi et benchmark er fastsat ved at overveje den øvre grænse (maksimal energigevinst gennem forbrænding). Ved at sammenligne det resterende energiindhold i gæringsprodukterne med de indgående stoffers energimix, præsenteres en specifik energieffektivitet, hvilket gør det muligt at anslå virkninger såsom forbehandling eller forlængelse af den hydrauliske opholdsperiode.

I den anden undersøgelse blev 34 fermenterings rester fra biogasanlæg undersøgt for deres grundparametre, GCV, rest metanpotentiale (BMP) og Klason lignin Content (tKL) for at forudsige forholdet mellem tKL og GCV og muligheden for at forudsige BMP med GCV. Der blev anvendt statistiske metoder til at finde tvær korrelationer. Multivariat og lineære modeller blev anvendt til dette formål. Resultatet af denne undersøgelse var imidlertid, at der ikke var synlige sammenhænge, og for det første, at Klason-metoden for gærings rester ikke blev udviklet, og for det andet, at GCV-metoden ikke var følsom nok til at forårsage mindre forskelle mellem brændværdi værdierne. af substrat blandingerne.

Ud over gæring kan biogasanlæg også drage fordel af forbehandlingen af biomasse til forbedret biogas/metanproduktion. Den tredje undersøgelse så på lav-temperatur madlavning som en omkostningseffektiv forbehandling metode til forbedret biogasproduktion fra hvede halm. Til dette formål blev hvede halm forbehandlet i vand/fermenterings rester ved forskellige temperaturer (293 – 372 K) og forskellige holdetider (30-60 minutter). Målet var at bestemme den højeste BMP ved at fjerne de beskyttende strukturer (såsom voks) for at muliggøre hydrolyse af materialet. Det bedste resultat blev opnået ved omgivelsestemperaturer. Generelt er det muligt at sige, at en øget BMP kan forventes på grund af denne forbehandling i vand. Denne effekt kan knyttes til to effekter. For det første, når kogning i vand, voks lag strukturer fjernes, således at Mikrobiologi er i stand til at nedbryde de beskyttede strukturer, f. eks cellulose. For det andet opløser forbehandlingen i vand de bundne salte fra strukturerne, og som følge heraf blev der opnået en højere BMP sammenlignet med forbehandlingen i fermenterings rester.

1. Introduction

1.1 Motivation

The change of the energy sector in the EU towards a renewable, sustainable system is one of the biggest challenges of the century. The emissions of greenhouse gases (GHG) and the supply of limited resources, such as fossil fuels, gas and coal, call for new pathways in the energy generation [1]. One opportunity, beside wind, solar and hydropower, is the energy supply from biogas, based on renewable resources and waste streams. In Germany and Denmark, biomass for heating and energy generation is one big part of the renewable system. The benefit of this system is that, based on the setup, the gas can be stored and used for energy production when needed. Gas upgrading plants can use the natural gas grid for storing the gas [2–4] For example, the German gas grid has a length of 511,000 km with an annual consumption (in 2016) of 95 billion m^3 (BMWI)[1].

[1] https://www.bmwi.de/Redaktion/DE/Artikel/Energie/gas-erdgasversorgung-in-deutschland.html

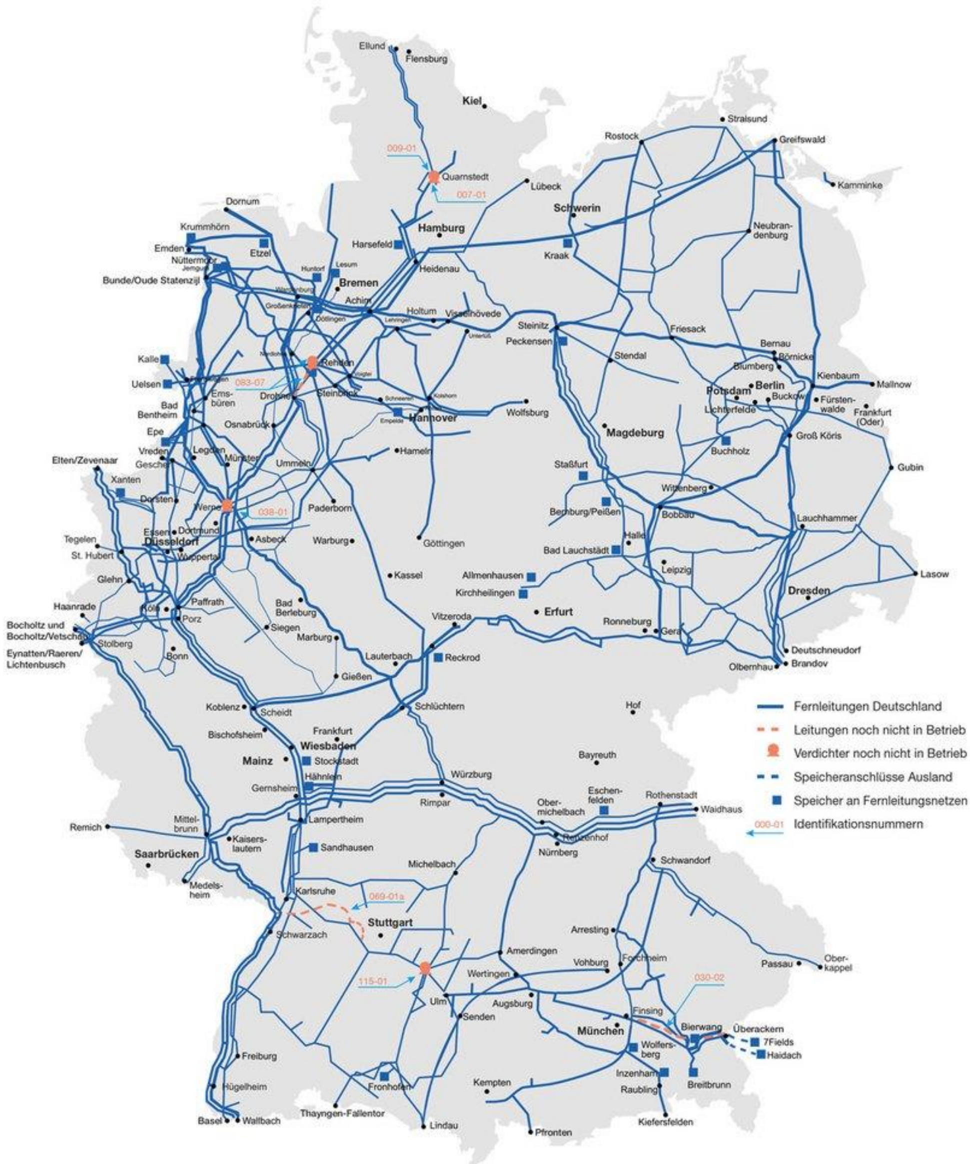

Fig. 1 German gas grid

As depicted in Fig. 1, the bioenergy production by anaerobic digestions can be used for decentral energy production with a centralized consumption.

On the one hand, biomass is highly available and has high energy contents. The generation of the needed masses for anaerobic digestion (AD) is accompanied with high emissions due to farming and storing. Agricultural waste streams have a significantly lower carbon dioxide footprint than energy crops, but also have a lower energy content which leads to higher amounts that is necessary for producing energy from them.

The EU has established the goal to reduce the greenhouse gas production by 2050 to 80 – 95% (Scarlat et al 2015). In 2015, the total biogas production in the EU reached 654-PJ of primary energy which is more than 18 billion m³ of natural gas equivalent, resulting from a development of the early 2000, where 92 PJ of biogas were produced. (EU statistics 2017, http://ec.europa.eu/eurostat).

However, today, biogas is mainly considered a first generation biofuel in Germany based on the fact that 77% of the gas is produced from energy crops which are only cultivated for biogas production. By this case, the energy production from cultivated crops has the lowest sustainability, thus for future energy production, based on renewable resources, new pathways should be considered to improve the image of biogas and for shaping a sustainable and economic future of RE production.

1. Utilization of waste streams for biogas production to overcome the food-to-fuel debate and lower energy production prices.
2. Usage of heat. Today, most biogas plants are installed outside of villages and towns and do not have any heat usage in addition to wood drying or Organic Rankine Cycle (ORC) energy production. Direct usage of the heat from CHP plants would increase the value of biogas production.
3. Gas upgrading and usage of byproducts. Since the gas grid has a large storage capacity, so that the energy can be produced where and when it is needed, gas upgrading is of increasing interest. Additionally, an approach is to eventually become independent of imported natural gas. Ultimately, the usage of carbon dioxide as a raw material for further processes (food and beverage industry or certificate trading) is a valuable option for existing biogas plants.

However, as we can see for example in Germany, the subsidies from the government have been reduced dramatically by the EEG of 2014 / 2017 compared to the subsidies from former EEG of 2004 / 2009. This general change in funding will be influencing the bioenergy sector based on biomass in the coming decades. The need for new, cheap resources as input materials for biogas production is an indicator of this change.

Generally, there are two obvious options for existing biogas plants to increase its profitability / not to encounter economic problems.

1. Reducing of input material costs by switching to residuals or by-products which have similar energy contents.
2. Increasing the gas production through repowering initiatives or pretreatment of the materials.

Nonetheless, it is all a question of profitability with the main question of how to measure the energy efficiency of the existing configuration.

Energy efficiency is expressed as the difference between input energy and output energy in a thermodynamic way [5]. A measuring system, based on independent factors, which also allows the comparison of each AD-system is needed.
Traditional methods for determining the energy efficiency are mainly based on:

1. Anaerobical digestibility through biomethane potential tests
2. Elementary compounds and empirically defined factors such as Weender-Analysis and FoDM-calculations

Gas potential tests, based on VDI 4630 [6], have the benefit that directly provide the available methane / biogas yield from the respective materials. However, the disadvantage of this method is that every potential test can be affected by several side effects – occurrence of trace elements [7–9], effects of the inoculum [10–12], temperature drops, testing failures due to operational faults. An elementary compound analysis offers the advantage, that it leads to the theoretical maximum of methane yield, but without taking into account the degradable and non-degradable portions of the materials.

This leads to the need for an independent evaluation method which takes into account the digestibility and the maximum methane potential.

1.2 Fundamentals of anaerobic digestion

AD is a biological process, where microorganisms convert biodegradable fractions of the input material into biogas – which is a mixture of CO_2, CH_4, H_2S and other trace gases. Furthermore, the microorganisms also produce microbial biomass and heat under anaerobic conditions.

Fundamentally, the AD process can be divided into four main stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Fig. 2 [5])

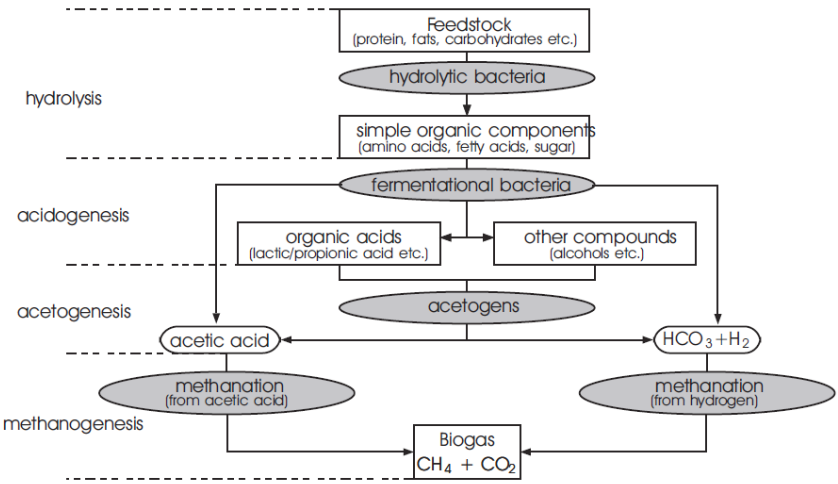

Fig. 2: Stages of anaerobic digestion by Kaltschmitt et. al. (2016)

The presented process stages take place simultaneously in the AD-process, for distinction they were placed in line. Each process stage has its individual micro-organism consortium which, in turn, has its own process optimum (physical, chemical and biological). The various steps of AD are highly complex and have to be handled with good biogas plant management.

1.3 Process stages

1. Hydrolysis

In the hydrolysis step, complex components from the feedstock are broken down to soluble monomers by hydrolytic bacteria. Mainly three components (carbohydrates, fats, proteins) are hydrolyzed into simple organic components, such as amino acids, long-chain fatty acids and sugars. The hydrolysis reaction is generally the rate-limiting step in AD processes of pre-digested materials such as manure or lignocellulosic biomass. The hydrolysis step is traditionally simplified to a single first-order kinetic reaction [13,14]. Therefore, it is necessary to extend HRT and use pretreatment techniques (physical, chemical or biological) to improve the enzymatic accessibility of the lignocellulosic substrates.

2. Acidogenesis

The second step in AD is the acidogenesis, where the hydrolyzed products metabolize into volatile fatty acids (VFA), hydrogen, carbon dioxide and alcohols [5]. Most agricultural substrates and residues are fermentable as it mainly consist of monosaccharides and amino acids.

Acidogenesis is generally a fast conversion step in the AD process, which can lead to VFA accumulation and the respective pH-drop when the following acid conversion steps are inhibited due to toxic compounds, low buffer capacity or fast temperature changes [5].

3. Acetogenesis

Following the acidogenesis, the acetogenesis is started where the produced acids and alcohols are converted by acetogens into acetic acid, carbon dioxide and hydrogen. This step takes place at the same time as the methane production, where the methanogens utilize the produced formate / hydrogen to produce methane. The produced hydrogen can also act as an inhibitor to the acetogenic bacteria [5].

4. Methanogenesis

As shown in Fig. 2, there are two pathways to produce methane from the given substrates. The acetic acid and the hydrogen pathway. The first group of bacteria (acetotrophic archaea) produce methane (CH_4) and carbon dioxide (CO_2) from acetate (CH_3COOH). The second group of bacteria (hydrogenotrophic archaea) produces CH_4 from H_2 and CO_2. Generally, the methanogenesis is the rate limiting step in AD processes, while the reproducing rate of the bacteria is very low. Also, the bacteria react sensitively to environmental changes (e.g. temperature or substrate changes, trace element occurence and inhibitors) [7–9] and can only convert relatively simple substrates [5].

1.4 Influencing parameters for AD processes

1. Temperature

The temperature is one of the most important parameters for the biological processes within AD. It directly affects the microbial activities. There are three main temperature ranges for AD – psychrophilic (< 25°C), mesophilic (25 – 45 °C) and thermophilic (45 – 60 °C) [5,15]

It has been observed that AD processes take place at 4°C on the ground of the sea, but psychrophilic digestion is not used for commercial biogas production due to low microbial activity and low biogas production rates.

For technical biogas production, mostly mesophilic and thermophilic temperatures are used. In Germany, most commercial scale biogas plants are operated under mesophilic conditions. In Denmark,on the other hand, nearly all biogas plants are operated under thermophilic conditions. Due to low exothermic processes during AD, there are benefits using mesophilic conditions based on lower heat demand to heat up the substrates to mesophilic temperatures. However, mesophilic AD requires 30 – 40 days to degrade the material in comparison to thermophilic AD which takes 11 – 14 days [16]. Based on the degradation time, financial benefits can be observed by using thermophilic conditions as it allows building smaller fermenters, and in connection with this, relatively short HRT are possible with the same methane yield. Additionally, thermophilic AD is able to inactivate the pathogenic organisms and thus increase the safety for agricultural use of the fertilizer. However, using thermophilic conditions leads to higher process monitoring demand because of higher sensitivity to environmental changes, process inhibitors (e.g. ammonia) and process fluctuations than mesophilic conditions [17].

2. pH – value

The pH – value is an essential parameter for AD. Each process step has its own optimum pH. For hydrolysis, the optimum is between 5 – 6.5, where as , for methanogenesis its between 7 – 7.5. However, biogas is still produced if the pH-value is close to the range of 7 – 7.5. These ranges apply to two-stage fermentation systems, where the pH optimum can be offered for each group. For one-stage fermentation systems, the pH-value is self-regulating and will end up in an pH-value between 7 – 7.8 [5,15]. A pH-drop in fermentation systems normally indicates an process inhibition or an VFA accumulation, but this is only valid for fermentation systems with low buffer capacity (e.g. mono-fermentation of sugar beets).

3. Volatile fatty acids

The volatile fatty acids are the main intermediate product of AD, which includes acetic acid, propionic acid, butyric acid and valeric acid and will be used by the downstream microorganisms as shown in Fig. 2 [18]. VFAs are not a direct inhibitor to the AD system, but the concentration determined as total volatile fatty acid content with titration or as separated concentrations via GC / HPLC can indicate a process imbalance [19]. The VFAs will accumulate in the fermentation system by rapid acidification in the first steps and will result in a pH-drop if the buffer capacity is low. However, one of the most common reasons for VFA accumulation is overloading the reactor but there are several other factors, which influence the system in the same way: e.g high ammonia concentrations, alteration of AD temperature, high hydrogen concentrations [5,15].

4. Ammonia

Ammonia is one of the most needed macro elements for AD processes next to carbon. During the AD process, ammonia is mainly produced by the degradation of nitrogenous materials, mostly present in the form of proteins and urea [20]. The total ammonia content is composed of the following substances: NH_3 and NH_4^+ ions. Free ammonia content increases concurrently with increasing temperatures and pH-values. Furthermore, high ammonia contents can be inhibitory for the methanogens [5]. However, bacteria are able to adapt to various habitat conditions but need long time for adaption. In most cases, these requirements do not correlate with the requirement of fast and efficient gas production from commercial scale biogas plants. At the same time, ammonia is buffer-active so that the higher concentrations of VFA do not result in an lower pH-value which is normally taken as an indicator for process-disturbances.

5. Carbon to nitrogen ratio (C/N)

Carbon is as nitrogen one of the most needed macro elements for microbial growth. However, AD systems are also sensitive to C/N ratios. Studies showed, that high C/N ratios lead to low biogas productions due to fast nitrogen degradation in the system. Systems with low C/N ratio increase the risk of ammonia as an inhibitory. It has been shown, that the optimal C/N ratio is between 20 – 30 [21–23].

6. Organic loading rate (OLR)

Volatile solids are the decisive factor for predicting the gas production and serve as quality parameter for substrates. The OLR represents the amount of volatile solids fed into the reactor per day under continuous feeding. High OLR results in high gas production rates but can also lead to process-inhibition due to high VFA production rates which, in turn, can lead to toxic acidification levels. With acidification, the equilibrium of hydrolysis and methanogenesis is interrupted and the pH-value decreases so that in single-stage fermenters the methanogens are not able to convert the produced VFAs into methane [5,21]. Literature values shows, that for CSTR the OLR is mostly between $2 - 4\ \frac{kg}{m^3 * d}$ and for Plug-Flow-Fermenters between $5 - 15\frac{kg}{m^3 * d}$.

7. Trace elements
Along with macro elements, microorganisms need micro elements (e.g. Fe, Ni, Mo, Co, W, Se) for their metabolic pathways and enzymatic reactions. There are no clear limits of trace element supply, but deficiency of macro- or trace-element supply can cause problems for AD stability. On the other hand, high levels can also lead to inhibitory or toxicity [8,9].

8. Retention time (HRT)
The retention time is the time which is required for complete degradation of the organic materials within the fermentation system. The retention time is connected / influenced with the microbial growth, OLR, temperature and substrate composition (e.g. fast degradable substances like sugar-beets or slow degradable substances like straw). The hydraulic retention time is defined as:

$$HRT = \frac{V}{Q}$$

where V is the available reactor volume and Q the daily substrate feeding. The retention time should be related to microbial growth so that not more bacteria are washed out of the system than are being reproduced and it also depends on the reactor type (Continuous Stirred Tank Reactor; Anaerobic Baffled Reactor; Plug-Flow; Batch Fermenter). Beside the HRT, the solid retention time (SRT) exists, which is defined as the time each particle spends in the system. Normally, for mesophilic conditions, the HRT is set to 30 – 40 days and for thermophilic conditions to 15 – 20 days [5,15,24]. In Germany, in relation to the EEG (Renewable Energy Sources Act 2002 – 2017), the gas tight covered time for biogas plants is 150 days and the total retention time is 180 days. In Denmark, there is no further gas tight storage planned after fermentation, so the fermentation residues leave the system after 25 – 30 days.

9. Total solids / dry material (TS / DM)
The total solids content is one of the main factors for designing the fermenters. Depending on the solid content, different fermenter types are available. These fermenter types can be divided into three groups. wet-digestion (< 10% TS), semi-solid-state (10 – 20% TS) and solid-state (> 20% TS). In Germany and Denmark most fermenters are designed as semi-solid—state digesters. This can be attributed to the usage of crops and manure for biogas production [15].

10. Digester types
Today, different types of fermenters are available, which all have their advantages and disadvantages and respective operation field which is explained well in literature [5,15,24]. Traditionally, most fermenters in Germany and Denmark are build up as Continuos-Stirred-Tank-Reactors (CSTR), but these types of fermenters are not able to digest all substrates without pretreatment or adding water to reduce the DM-content. However, most fermenters are designed for treating wastes with low DM-content and without large particles (e.g. waste water from industries). Thus, it is important to optimize the digester type. Furthermore, pretreatment (e.g. chopping, milling etc.) for fibrous-substrates is necessary.

11. Input Materials
Generally, there are two main input material streams for commercial AD-proccesses present.

Firstly, cultivated crops with high energy content as Maize, Gras, Sugar-Beets, which can be harvested and stored with the known procedures and machines of the agricultural sector. These input materials does have several benefits, which are partly presented in the following:

1. High energy and DM content e.g. of Maize-Silage
2. Easy and cheap in cultivation

3. Well known and well developed methods for harvesting and storing
4. Low process influences e.g. by using Maize-Silage related to VFAs, DM, Inhibitors, C/N-Ratio

But there are also disadvatages by using these materials such as:

1. Potential food as feedstock for energy production
2. High energy and fossil fuel consumption for nutrient supply (e.g. Nitrogen), cultivation, harvesting and storing

As second input stream for biogas plants agricultural by-products and leftovers are used (e.g. manure). These materials must not be conserved but also have gas losses related to post-warming and pre-AD in the storage tank. But, using these materials has several benefits:

1. Environmentally friendly; usage of manure to produce energy out of it before usage as fertilizer has a positive impact on the environment
2. Pretreated material by pre-fermentation in the stomach of the respective animal and also adapted bacteria for fermentation are present in the material
3. Micro and macro element supply: With manure and other by products several micro elements (trace elements like heavy metals – which are necessary for complete and efficient degradation of the materials) and macro elements (e.g. nitrogen, phosphorus, magnesium) were supplied to the fermentation system.

However, there are also disadvantages present when using these materials:

1. Low gas quantity by pre-fermentation in the animals – this leads to high input streams for relevant gas production
2. Losses by post-warming while storing the materials
3. Potential inhibitors (e.g. high nitrogen content which converts into NH-3 during fermentation, antibiotics or antibiotically active substances)
4. Low VS content and abrasive effects to concrete and stirrers

As third input stream biological wastes can be used for AD, but this is not part of this Thesis.

1.5 Mass and energy balances with uncertainties at large scale plants

At present, most biogas plants – in the observed regions for this Thesis – are agricultural related. This means, that they built up as farm scale (≤ 75 kW of electric power) or large scale (> 75 kW of electric power or gas upgrading plants) and owned by farmers, project companies of farmers and investors or energy suppliers. Traditionally, most biomass is delivered by truck or tractor to the biogas plants and weighted on a calibrated balance at the respective biogas plant.
Therefore, the deliverers of the input materials directlly know the mass delivered and can invoice accordingly.
By storing the materials, losses will appear, which normally have an influence to the Mass- and Energy balance of the plant, but can not be taken correctly into account. The potential losses and influences are presented in the following shortly.

1.5.1 Losses at large scale plants

For conservation and storage of the cultivated plants, e.g. maize silage, the harvested material is stored mainly in silage heaps, where two films are applied:
one oxygen-barrier and one weather protection film.

1. The oxygen-barrier film is mainly produced from polyamide or ethylene-vinylalcohol-copolymer. By applying this film, losses of DM (by post warming) in the surface near region of the silage (up to 50 cm depth) can be reduced [25–27]. The second task of these films is to accelerate the acidification process by additionally added homolactic bacteria while harvesting to obtain a stocking with the desired bacteria and to avoid a false fermentation [28–30].

2. The weather protective film is obviously applied to protect the harvest from rain and other weather influences. Due to silage process, leachate water and dry-material losses appear, which should be as low as possible by correct storing and taking from the heap.

In the second step, the material is dispatched from the silage heap or pumped out of the tanks for fermentation. During fermentation, several specific and unspecific losses are present, which are partly listed below:

1. Losses due to permeation through the roof foil. These losses can be theoretically calculated by the permeation factor from the respective foil and the present pressure in the system. However, these factors are only valid for a brand-new foil and not one which has stretched thousands of times by changing pressures and filling levels of the gas storage system [31].
2. Losses due to permeation through the concrete walls of the fermenters. There is no clear number available for determining the masses, so a calculation of the losses is not possible [32].
3. Losses while using the gas in CHP-plants or for biogas upgrading. Using a CHP-plant for conversion of chemical energy into mechanical energy, several losses by friction of the pistons and other moving components appear, also losses related to incomplete burning – slipping of gas – can be found in literature. For gas upgrading plants slippage and incomplete separation of the gas are the main losses [32–35]
4. Losses through pipes, connections, safety-valves and stirrers [32,34,35].

However, next to technical losses, biological losses are present. To cover their energy demand, microorganisms degrade biological products like acetate or glucose. As a by-product, biogas is produced. In the end, up to 7% [5] of the input material will be converted into biomass and is no longer available for methane production.

1.5.2 Balance borders at commercial scale biogas plants

To determine the energy efficiency, with the previous presented losses and self-consumption of the bacteria, a correctly set balance borders is necessary.

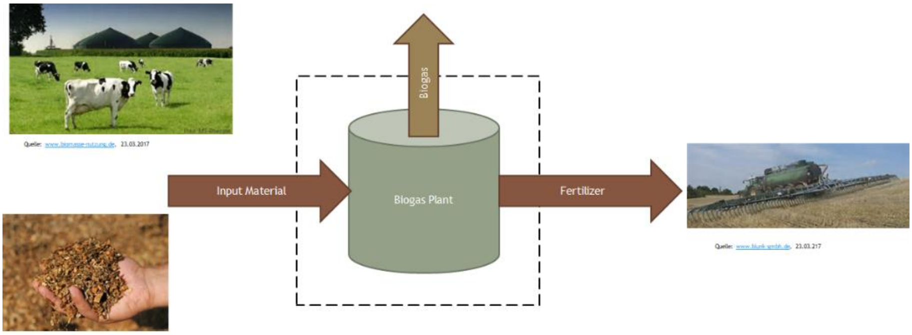

Fig. 3 System boundaries

As shown in Fig. 3 , the balance limit is set for the whole biogas plant. The material storage and fertilizer removal are excluded from this balance. Thereby, the losses relating to the storage of the input materials are not included in the system boundaries and do not directly affect the energy efficiency. By using this system boundary, all losses during fermentation and gas usage are included.

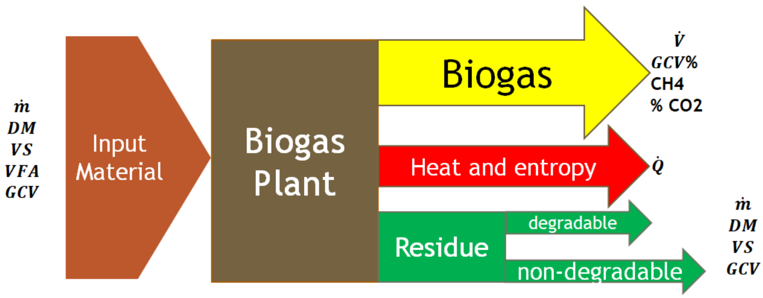

Fig. 4 Mass- and energy flowchart

As shown in Fig. 4 by applying the boundary, all needed production and output-streams are considered for further analysis.

2. Energy efficiency of commercial scale biogas plants

2.1 Background and classic energy efficiency

In conventional power plants energy efficiency is recovered by thermochemical conversion of the fuels. In most cases the energy content of the fuel is converted into usable energy through several stages. The conversion of energy is necessary because the primary energy content of natural products is often not usable for technical purposes.

Depending on the type of the power plant, the efficiency is defined by

$$\eta = \frac{-P}{\dot{m}_B * GCV}$$

$$-P = rated\ capacity$$

$$\dot{m}_B = daily\ input\ of\ substrate$$

$$GCV\ = Gross\ calorific\ value\ of\ the\ material$$

Given that, a certain amount of energy would be required to enable conversion to electric power $-P$, η becomes the net efficiency of the power plant [36–38].

The maximum energy content of the fuel which becomes available by complete oxidation can be expressed by elemental analysis of the usual elements, i.e. analysis of (C, H, O, N, S) [39,40]. This is because every fuel has its specific elemental composition and specific energy content which often becomes available by complete oxidation.

2.2 Empirical calculation models

In case of biomass, the calorific value can either be estimated by empirical equations [41–46] or by laboratory experiments.

The most applicable equation for estimating the calorific value by its elemental compositions seems to be the methods of Scheurer and Wilson, by its development for municipal solid

waste and by application of these formulars for prediction of the GCV of Lignin realistic values were achieved (e.g.Lignosulfonate Lignin = 16.84 – 18.65 kJ/kg). Additionally, it has to be clarified, whether all calculation equations are developed for municipal waste or fossil fuels.
However, the methods of Scheurer and Wilson [46] are notated in the following:

$$GCV = b_C * m_C + b_H * m_H + b_N * m_N + b_O * m_O + b_S * m_S$$

$m_C = mass\ of\ elemental\ carbon$
$m_H = mass\ of\ elemental\ hydrogen$
$m_N = mass\ of\ elemental\ nitrogen$
$m_O = mass\ of\ elemental\ oxygen$
$m_S = mass\ of\ elemental\ sulfur$

Name	b_C	b_H	b_N	b_O	b_S
Scheurer	339.1	1027.9	0	-75.4	94.2
Wilson	327.9	1608.2	-24.2	-151.3	92.6

Tab. 1 Correction factors Scheurer and Wilson

However, the ash content is not taken into account, because it has no energetic relevance. These empirical methods are not suitable for fresh material (e.g. cultivated plants or agricultural leftovers) and lead to a high laboratory work to analyze the components.

2.3 Classic GCV laboratory method

In order to be able to assess / analyze the efficiency of the biogas plant using a similar method analogous to the power plant technology, the energy assessment of inputs to the biogas plant has to be accounted for. For this, the determination of the GCV according to DIN 18125:2017 [47] is used and adapted.

Generally, the samples of the input and output materials (see Fig. 4) are dried and pelletized before being used in a bomb calorimeter to determine the calorific value. For the energy content with reference to the calorific value, the following equation applies:

$$GCV_{measured} = \frac{Q_{measured}}{m} = cp * \Delta T$$

$Q_{measured} = measured\ heat\ of\ combustion$

$m = mass$
$cp = specific\ heating\ capacity$
$\Delta T = measured\ temperature\ difference$

In order to comply with thermodynamic laws, the oxidation of the biomass must be fully considered. Thus, the following equation is used:

$$GCV_{measured} = q_{usable} + q_{biomass} + q_{unused}$$

with:

$$q_{biogas} = energy\ content\ of\ biogas\ related\ to\ methane$$
$$q_{biomass} = specific\ demand\ of\ the\ bacteria$$
$$q_{unused} = unused\ degradable\ biomass\ and\ inert\ components\ like\ lignin$$

The specific system consumption of energy associated with the overall processes is considered to be about 7% [5] (see. 1.5.1) of the total energy content of the biomass. This implies, that 93% of the total energy content are available for AD processes. In this, the energy content of lignin is included, which is anaerobically non-degdrable.

Using fermentation residues, the equation is simplified to:

$$GCV_{measured} = q_{usable} + q_{unused}$$

Where q_{usable} is the most interesting part as being an energy efficiency indicator.

2.4 Correction factors

The application of correction factors in the GCV method is necessary as most substrates contain nitrogen and sulphur. These components are converted by complete oxidation into sulphuric and nitric acid. Therefore, the correction of the GCV value is as follows:

$$GCV_{biomass} = GCV_{measured} - (q_N + q_S)$$

The specific enthalpy for the formation of sulphuric and nitric acid are obtained with reference to the literature [47].

Sulphur → Sulfuric acid	0.094 MJ/kg per mass-% S
Nitrogen → Nitric acid	0.043 MJ/kg per mass-% N

Tab. 2 GCV nitrogen – sulpur

Literature of the fermentation residues shows values of nitrogen and sulphur content in the samples – these values cannot be universally used as every biogas plant uses different substrate compositions [48,49].

	Digestate	Separated digestate [l]	Separated digestate [s]
DM [%]	8.39	5.45	26.71
N [g/kg]	7.02	6.92	9.38
S [g/kg]	0.48	0.38	1.53

Tab. 3 Mean Literature values of N / S content in digestates [50]

By applying these values, the following correction factors for digestates are possible:

Residue type	Correction factor
Digestate	0.35 MJ/kg FM
Separated digestate [l]	0.33 MJ/kg FM
Separated digestate [s]	0.55 MJ/kg FM

Tab. 4 Correction factors for digestates

In addition to fermentation residues also correction factors for cultivated biomass and agricultural leftovers have to be described. In the following, the mean literature nitrogen content of the most used input materials and their respective correction factors are summarized.

	DM [%]	N [g/kg]
Cattle dung	25	7.1
Poultry manure	45	16.9
Chicken manure	50	28.6
Cow manure	12	5.7
Pig manure	8	7.5
Maize silage	28	4
CCM	60	10
Rye silage	35	7
Sugar beets	23	1.8

Tab. 5 Nitrogen content of common substrates

Applying these average nutrient contents for conversion into nitric acid, the following average correction factors are given.

Type	Correction factor
Cattle dung	0.31 MJ/kg FM
Poultry manure	0.73 MJ/kg FM
Chicken manure	1.23 MJ/kg FM
Cow manure	0.25 MJ/kg FM
Pig manure	0.32 MJ/kg FM
Maize silage	0.17 MJ/kg FM
CCM	0.43 MJ/kg FM
Rye silage	0.30 MJ/kg FM
Sugar beets	0.08 MJ/kg

Tab. 6 Correction factors of biomass and leftovers

In order to be able to calculate a complete energy accounting for the considered biomass, it is necessary to correct the GCV of the input materials to the respective content of VFA which are partly lost by oven-drying. These volatile substances (alcohols and acids) can be metabolized by the microorganisms into acetic acid, which can be converted into methane.

The conversion from acetic acid into methane is given by:

$$C_2H_4O_2 + 2H_2O \rightarrow 4H_2 + 2CO_2 \rightarrow CH_4 + CO_2 + 2H_2O$$

In the first degradation step the mircoorganisms require 104 kJ/mol, in the second step 135 kJ/mol is generated. Thus, the total released energy is 31 kJ/mol.

For the hydrogenotrophic pathway, the conversion is given by:

$$4\,H_2 + CO_2 \rightarrow CH_4 + 2H_2O$$

In this case, the released energy is 131 kJ/mol. In general, the hydrogenotrophic pathway is energetic more favourable for bacteria, but in most digesters, more bacterias are present, which use the acetic acid pathway.

For practical usage, Weissbach et. al [51,52] investigated the specific losses of VFA during oven drying for the DM analysis, the results are recorded in Tab. 7.

	Maize-silage [g/kg FM]	Volatile factor [%]	Gras-silage [g/kg FM]	Volatile factor [%]	Sugar-beets [g/kg FM]	Volatile factor [%]
Acetic acid	9.98	95	8.27	78	7.74	95
Propionic acid	0.28	97	0.45	78	0.04	95
Isobutyric	0.01		0.19	84	0.52	95
Butyric acid	0.09	100	2.06	88	0	95
Isovaleric	0.06	-	0.36	71	0.08	95
Valeric acid	0.01	-	0.1	93	0	95
Caproic acid	0.01	-	0.19	92	0	95
Lactic acid	15.2	7	14.63	10	11.95	8
Methanol	-	-	-	-	1.25	100
Ethanol	5.8	100	2.5	99	37.18	100
Propanol	0.25	100	0.2	100	0.09	100
Butanol	0		0.01	100	0	100
1,2 Propanediol	0.7	77	0.6	77	0.26	100
2,3 Butanediol	0.08	100	0.26	87	0.49	100

Tab. 7 Volatile alcohols and acids in biomass

In consideration of the standard enthalpy of the acids and alcohols and also their volatility, the correction factors are given in Tab. 8.

Silage	Correction factor
Maize silage	0.34 MJ/kg FM
Gras silage	0.27 MJ/kg FM
Sugar beet silage	1.43 MJ/kg FM

Tab. 8 Correction factors of biomass

By adding these values to the GCV method, the equation changes to:

$$GCV = GCV_{measured} - (q_N + q_S) + q_{VFA}$$

With this, the total energy efficiency of AD-plants, with considering the time, can be defined as:

$$\eta = \frac{\dot{q}_{Input} - \dot{q}_{Output}}{\dot{q}_{Input}} = \frac{\left(\sum_{in}(\dot{m}_{in} * DM_{in} * GCV_{in} - (\dot{q}_{N,in} + \dot{q}_{S,in}) + \dot{q}_{VFA,in}) - \sum_{out}(\dot{m}_{out} * DM_{out} * GCV_{in} - (\dot{q}_{N,out} + \dot{q}_{S,out})\right)\right)}{\sum_{in}(\dot{m}_{in} * DM_{in} * GCV_{in} - (\dot{q}_{N,in} + \dot{q}_{S,in}) + \dot{q}_{VFA,in})}$$

The presented correction factors only serve as an overview: In Paper 1 the literature values were used, in Paper 3 the measured values of VFA and nutrient concentrations were used.

2.5 Batch fermentation tests

Biological degradation of biomass is mostly performed by BMP-tests [53], where a inocolum as a starter culture as initial starter for degradation is added. The inocolum is in most cases sewage sludge from a municipal waste water treatment plant. According to VDI 4630, the inocolum and the sample is mixed (VS based 50:50), placed in a water bath at 38°C and the gas produced is measured. The fermentation test is considered complete, when the gas production rate is lower than 0.5% of accumulated gas production.
Batch fermentation tests are simple, easy to set up and allows for simplistic monitoring and evalutating the gas/methane production of nearly all biological materials.
A determination of the degradation efficiency is possible with batch test, if the fermentation residue is also tested. But the maximum methane production depends on several influencing

factors like grain size, trace element supply, possible inhibitors (e.g. Nitrogen) so that a general statement about the degree of conversion is not given.

2.6 Dry Material – Volatile Solids calculation

The DM and VS [54] are basic parameters for describing the water content and the organic material content of a sample. With these parameters a description of the degradation of organic materials (i.e. material which is converted into biogas) can be made. Taking into account, that a small fraction of the organic material is used for bacterial growing (See Paragraph 1.5.1), whereas the substantial portion is converted into carbon dioxide and methane, an efficiency can be calculated. Utilizing standard tables for calculating the methane content, while digesting the samples [15,24], a description of the energy content is possible. Moreover, modeling a mass balance is possible by comparing the DM content of the input and output of the system. Modeling an energy balance is not possible with this method, based on the unknown portion of VS which is converted into biomass.

2.7 FoDM - calculation

The fermentable organic dry material (FoDM) calculation method of Weissbach [51,52,55], is an extended VS method for describing the fermentable organic materials. This method allows for an estimation of the gas production of several different input materials. Furthermore, the correction of the VFA in the organic material is ncessary, as these components are partially vaporized during the oven drying at 105°C. However, with this equation it is possible to predict the biogas production in an easy way without considering the biological parameters within the fermentation.
This method in combination with the GCV is used by Fischer et. al. [56] for building mass and energy balances on biogas plants, but this method does not consider the residual biologically degradable energy content in a reliable way, on the account that the FoDM is based on estimations and not on reproducible

measurements and the lignin content is not considered for AD-efficiency.

2.8 Time series analysis

For the correct determination of the energy efficiency, different influencing factors must be taking into account which are present in biogas-plants and which are more or less influential. The most significant are presented in the following:

- Material quality changes in the silage heap
- Quality changes of the agricultural leftovers
- Incomplete mixed tank reactor
- Error of sample taking and measurement errors

Furthermore, related to long HRT of the plants (> 150 days), this results in a considerable time difference between measurement of the input- and output materials.
However, next to the given demands for time series analysis, other side effects become visible while applying this method:

- Influences and quality of process management
- Effects of repowering initiatives and / or pretreatment technologies
- Recurring regularities / irregularities while fermentation
- Seasonal fluctuations (e.g. rainwater intake)
- Smoothing of measurements outliers

With consideration of the influencing factors and possible benefits, the investigation period was set at least to two HRT of the plants.

In the following, the basic data of the for Paper 1 investigated biogas plants are presented.

Investigated Biogas Plants					
	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5
Fermentation Volume	8,000 m³	5,800 m³	4,400 m³	14,200 m³	11,300 m³
Retention Time	96 d	70 d	118 d	184 d	134 d
Materials	Renewable Resources / Manure	Renewable Resources / Manure	Renewable Resources / Manure	Renewable Resources / Manure	Renewable Resources

Tab. 9 Investigated plants of Paper 1

However, the main idea of time series analysis for commercial use was to develop a management system based on GCV as efficiency indicator (See Paper 1), which allows fast prediction of the total energy efficiency and anaerob inacessible portions (See Paper 3). With consideration of the GCV, the lignin content should be described and a comparision with other biogas plants with the same design or same input materials should be possible. Based on these ideas a clustering of biogas plants is feasible and regularities could be found. The main disadvantage of this method is, that long measurement periods are necessary to determine the efficiency and for smoothing the recurring influences like substrate changes, rainwater intake.

3. Papers prelude, perspective and discussion

3.1 Papers Prelude

The aim of this thesis was to develop and evaluate an independent efficiency measuring method for commercial scale biogas plants method based on the GCV of the input- and output materials. The method should have the following advantages over established methods (e.g. biomethane potential tests):

1. Independence from process variables (e.g. inoculum, temperature, HRT etc.)
2. Fast, replicable and reliable results
3. Cheap and easy to use

For this five / seven commercial scale biogas plants located in Schleswig-Holstein and southern Denmark were investigated within a one / two-year-time-series-analysis.

The work conducted during the Ph.D. period can be divided into three topics.

Basic research and laboratory experiments: In a detailed study the GCV methodology was investigated for applicability on biomass and especially for describing the energetic efficiency of biogas plants. The methodology and first results based on a time-series-analysis had been published in Paper 1.

Cheap and easy pretreatment: Experiments covering mechanical and thermal pretreatment of lignocellulosic biomass for enhanced biogas production have been performed during the Ph.D. period. Laboratory experiments focusing on a cheap and easy pretreatment method for substituting e.g. maize silage by agricultural leftovers such as wheat straw, at low temperatures (< 100 °C) had been summarized in Paper 2.

Anaerobic inaccessible portion of fermentation residues: Detailed research on the anaerob inaccessible portions within the fermentation residues had been investigated with the Klason-Lignin extraction method. Results and statistical investigations to find correlations had been published in Paper 3.

Based on the research, the need for further investigations and basic research of Lignin-Determination in relation to anaerobic inaccessible parts of fermentation residues could have been shown.

3.2 Discussion and Perspectives

In the future biogas will be needed for balancing electrical grids and to supply a new generation of biofuels (methanol, Bio-LNG). In combination with surplus wind energy the generation of hydrogen for the dynamic upgrading of biogas will present anopportunity. The foundations have already been laid by the RED-II (EU 2018/2001) directive of the EU, where the goal of 32% of renewable energies in the energy sector is bindingly specified.
In Denmark for example, by July 2018, 18.6% of the natural gas demand was covered by biogas.
On the other side, biogas in Germany is close to a dead end and the market has to transform fast – from cultivated crops to manure and agricultural by products. Therefore, the nitrate directive of the EU (91/676/EWG; 2013/17/EU) is, based on the lawsuit against Germany, implemented in the current version of the fertilizer directive (Düngeverordnung, 2017/05/26) which is currently under revision by the European parliament.
However, biogas can supply sustainable energy and can play a significant part in achieving the climate protection targets.
As a first step, the energy efficiency of each commercial scale biogas plant should be monitored, the total energy efficiency can then determined with the GCV method presented in Paper 1.

Thanks to this monitoring, every plant owner could directly see how his energy exploitation is and it would allow to predict the economic viability of repowering initiatives or substrate changes.
Secondly, the presented method of Paper 1 and Paper 3, must investigated and taken into revision to determine the anaerobic non-degradable parts of the substrate mix. For this, the prediction model based on Klason-Lignin and GCV seems not to fit.

The following describes the method presented in Paper 1 for modeling the energy efficiency:

Based on the laboratory investigations, by applying assumptions:

- Fermentation residue is a two-component mixture of lignin and cellulose, the water is not taken into account as it has no energy content
- Lignin in fermentation residues has an GCV of 28.6 kJ/g
- Carbohydrates (Cellulose) has an GCV of 17.4 kg/g

Applying these assumptions to an model, the following picture can be drawn.

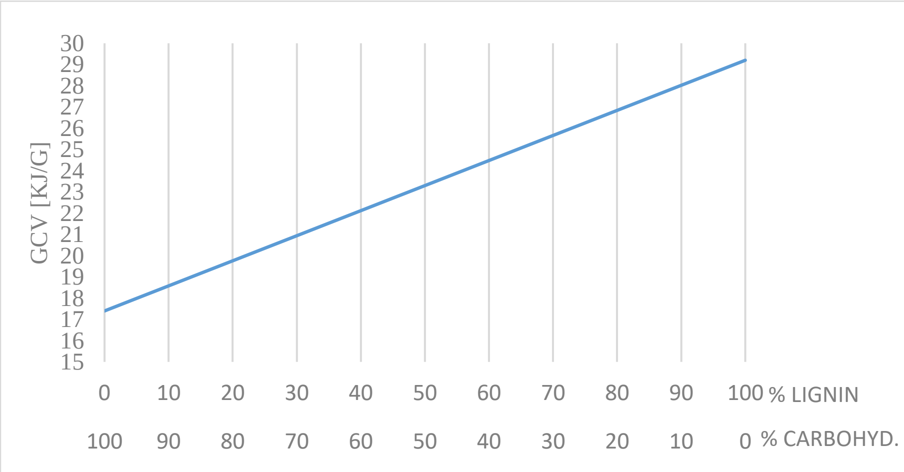

Fig. 5 GCV Lignin – Carbohydrates

With the significant differences between the GCV of lignin and carbohydrates, a simple equation for prediction of the lignin content can be modeled.

1. $$x_C + x_L = 1$$

2. $$x_C * GCV_C + x_L * GCV_L = GCV_{Substrate}$$

3. $$x_L = \frac{GCV_{Substrate} - GCV_C}{GCV_L - GCV_C}$$

With:

$x_C = Mass\ portion\ of\ Cellulose$

$$x_L = Mass\ portion\ of\ Lignin$$

The approximately determined portion of lignin, based on simple investigations of the substrate, allows to describe the unused but anaerobically digestible part of the lignin portion.

The lignin corrected efficiency is determined as:

$$\eta_L = 1 - \frac{GCV_{Res} * \ DM_{Residue} * x_{C,Residue}}{GCV_{Substrate} * \ DM_{Substrate} * x_{C,Substrate}}$$

With these findings, a modeling of the total energetic efficiency of the plant seems possible, with uncertainties related to e.g. measurement- and sample taking errors.
Applying this method, without lignin correction, to existing plants, results in the following graph.

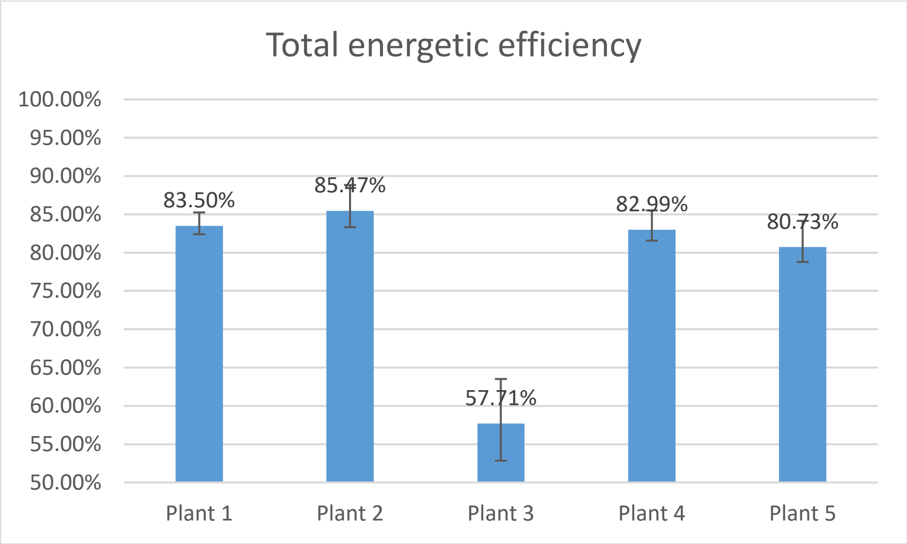

Fig. 6 Total energetic efficiency plants Paper 1

By applying the equation including the anaerob inaccessible portion of lignin, the results changing significantly.

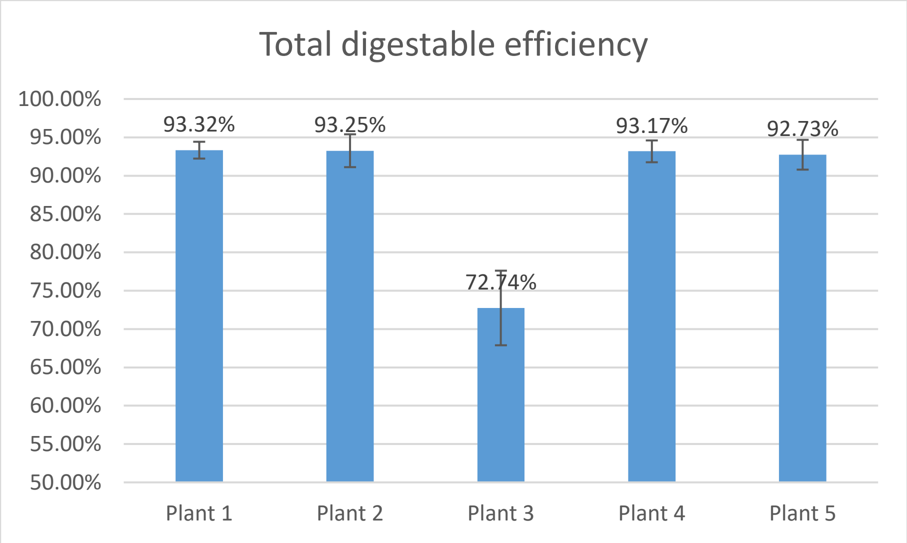

Fig. 7 Total digestable efficiency plants Paper 1

However, without lignin correction, the energetic efficiency was in the range between 57.7% - 85.5%. With lignin correction, the digestable efficiency was between 72.7% - 93.3%. The presented error bars are the standard deviation.

Nevertheless, the presented method can provide plausible and with correct monitored input parameters (amounts of substrate, digestate) comparable and correct results. But, based on the investigations of Paper 3, the lignin determination should be focussed much more in the future to provide correct GCV for prediction and modelling. Also, only time series analysis allows reliable statements about the efficiency of biogas plants, singular or random measurments are only highlighting one moment and does not show alterations or influences to digestions. In the end, with this method economic statements related to substrate changes e.g. from cultivated maize silage to poultry manure can be made by comparing the energy content of each input material in an fast and easy way compared to e.g. BMP – Tests.

Perspectives:

The next valuable step for biogas should be a shift of paradigm. Nowadays, biogas almost represents a second income for farmers based on energy production or substrate delivering (in Germany). In order to make a positive contribution in the future, the Danish-models should be taken into account more frequently. In the last years in Denmark biorefineries were build up e.g. the Maabjerg biorefinery in Holstebro or the Billund biorefinery. In these cases, AD is used as a problem solver for nutrient overloading by the heavy agro-industry in the region – this way of thinking should be transported into the minds, using all available resources to generate values and not waste.

Also new pretreatment technologies have to be considered - today most pretreatment is based on high energy demand systems [57,58] (electrical or thermal – e.g. hammer-mills have around 50 kW of electrical-consumption and steam-explosion needs temperatures about 473 K and pressures of around 10 - 15 bar) and for these cases the energy must be produced and cannot be covered by surpluses or unusable, low temperature streams. Light cooking of e.g. straw in combination (See Paper 2) with e.g. poultry manure offers new pathways for biogas production. Both streams are broadly availabe and currently inexpensive. With low-cost thermal pretreatment no highly engineered, specialized and expensive pretreatment technologies are needed. After AD a carbon and nitrogen rich product can be generated which can then be upgraded.

For fertilizers, new optimized possibilities are currently being investigated e.g. pyrolysis or HTC [59,60]. For pyrolysis, the residue is separated into a liquid and a solid phase. After separation the solid residues are dried and pyrolyzed (450 – 650 °C). The generated biochar has, related to the carbon content of the fermentation residues, a quality which allows further usage. There are several, interesting application fields for biological char:

- Nutrient recovery by usage as filter material for the liquid phase
- Soil improver by direct usage of the char as carbon-source
- Peat substitute through the use of additives and fermentation
- Water cleaning by usage as filter material
- Healthcare service for animals as feed-additive

For HTC – coal the fermentation residue is heated up to 250 °C in a closed pressure reactor (approx. 40 bar). The generated hydrochar can be used directly as soil improver with high nutrient recovery.
These presented opportunities are only two of several research fields for digestate upgrading. The application of these would lead to environmental services by the agricultural sector without losing the efficiency of mass livestock farming.

Also, as presented in Paper 5, the dynamic biogas upgrading with hydrogen, produced from surplus wind energy is a valuable and sustainable way to produce RE in alignment with the available resources.

Future research:
In order to accelerate the practical implementation of the time series method beyond the laboratory phase, further research would be required in the following areas;

- analysis of the usable energy content of residues, especially for waste treatment plants with heterogeneous mixtures.

- Enlargement of single processing steps to analyse the single elimination rates of the components in the mixture. In this case, mono fermentation systems can be used to obtain information related to conversion factors.
- Adaptation of the time series method to include leachate water and surface water running off, which is affecting the residue quality.

This could be achieved by obtaining universal correction factors for specific biomass based on plant locations.

To obtain complete information in relationship to the fermentation process and the required retention time of substrates, adaptation of the time is necessary. Reference can be made to the fact that the observation period should be at least three times the hydraulic retention time of the system analyzed.

3.3. Conclusion

The presented GCV method is suitable for computing the balancing of biogas plants and to show up the total efficiency of the monitored plant. The method is not usable to define individual efficiencies of the single processing levels in standard biogas plants with continuous stirred tanks reactors. Case in point, definition of gas losses by permeation through the roof and losses associated with the burning of biogas in the CHP- or gas upgrading unit cannot be represented with this method so far.

A definition of the usable residual energy is only possible for plants with cultivated biomass and animal by-products, it is not possible for plants that rely on waste as substrate. In addition, there are several uncertainties which results in a very low R^2 (see Paper 3) for prediction. Furthermore, the definition of the required retention time for complete degassing of the biomass cannot be obtained with the present method.

With reference to the time series analysis, it can be observed that aspects such as changing the process management, repowering initiatives and changing of the substrate qualitatively influence the total efficiency of the biogas plant. In addition, the time series analysis method is quick and easy to use and does not require long time periods as is the case for batch fermentation tests often used.

Due to the absence of relevant measuring instruments to carry out relevant basic tests at most biogas plants, a total balance of the residues is often not feasible This is especially the case because certain factors influence the quality of the residue. These factors include;

- Reduction of residue quality by drained leachate water from poorly stored biomass
- Exposure of silage to contaminated water from rainfall for instance
- Residue output without measuring

Due to the influential factors highlighted, the total efficiency of the probed biogas plant could be overestimated, exposing the need for further research.

Basic research and laboratory experiments

Paper 1 - Lignin Analysis Methods – Usage as efficiency indicator for commercial scale biogas plants in comparison with traditional methods

Authors: René Casaretto, Fritz Thomsen, Jens Born, Jens Bo Holm-Nielsen

Status: Published in Bioresource Technology Reports, 7 (2019)

Abstract

The energy efficiency of biogas plants is fundamentally based on the biochemical degradation of input materials. This paper introduces a novel method of efficiency determination based on the gross calorific value (GCV), a very common method in conventional power generation. GCV investigation of five commercial biogas plants in northern Schleswig Holstein were conducted by a one-year time series analysis with weekly sample taking. Although initially a simple model was used to estimate the lignin content, the plausible results indicate the suitability of the proposed method. For comparison, methods like the FoDM and the classical biomethane potential test are highlighted to point out their traditional usage and their adaption for the biogas sector. Also the laboratory efforts they cause is taken into account.

Paper 4: Comparison of biogas plants by their input materials and plant design

Authors: René Casaretto, Jens Born, Jens Bo Holm-Nielsen

Status: In Prepararation – Draft

Abstract:
Danish and German Biogas Plants differentiate significant by their design and temperature level. For describing and comparision of biogas plants gross-calorific-value investigations for independent energy monitoring were performed. This paper compares seven different large scale biogas plants located in northern Germany and southern Denmark by design, input materials and energy efficiency. For this, the plants were monitored in a two-year time series analysis from 2016 – 2018 with monthly or two-weekly sampling. Benefits of manure digestion and co-digestion of renewable resources were compared with the greenhouse gas reduction level and economic effects.

Cheap and easy pretreatment

Paper 2 – Low temperature pretreatment of lignocellulosic biomass for enhanced biogas production

Authors: René Casaretto, Tanmay Chaturvedi, Emil Brohus Lassen Agdal, Aadila Cayenne, Jens Born, Jens Bo Holm-Nielsen

Status: Submitted to Chemical Engineering & Technology

Abstract:

The usage of readily available lignocellulosic biomass as substrate for biogas plants is gaining popularity amongst biogas plant operators. This paper describes the results of low temperature pretreatment (light cooking) of wheat straw to remove waxes and prepare the biomass for microbial action. Benefits of light cooking are, low thermal energy demand and low investment cost compared to conventional techniques such as steam explosion. For investigation two different types of wheat straws were pretreated at varying temperatures and sizes. Results were conducted by biomethane potential test. The results were compared with Buswell's equation for theoretical maximum Biomethane yield.

Anaerob inaccessible portion portion of fermentation residues

Paper 3 – Examining anaerobic biodegrability of digestates – influence and correlations for Klason-lignin

Authors: René Casaretto, Torsten Mächtig, Christian R. Moschner, Eberhard Hartung, Jens Born, Jens Bo Holm-Nielsen

Status: Submitted to Chemical Engineering & Technology, Revised with the comments of the Reviewer in 08.2019

Abstract:

Appropriate evaluation of process performance of biogas plants needs to consider anaerobic biodegradability of the used biomass. This biodegradability is limited by lignin, which is part in most substrates and digestates of biogas plants. Previous research has shown, that the content of acid detergent lignin in digestates can be predicted from measured gross calorific values (GCV). The present study evaluates the correlation of GCV of digestate samples and its Klason-lignin (KL) content. Also correlation of KL content and other components to residual biomethane potential (BMP) is examined. Results show low correlation of chemical composition to GCV and BMP. Concluding from the results, evaluation of biodegradability of biomass by measuring KL or predicting KL from GCV is not productive.

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